(19) Patent Office of Japan (JP)
(12) KOKAI TOKKYO KOHO (A)
(11) Laid-open Application Number: 2001-202956 (P2001-202956A)
(43) Publication Date: July 27, 2001

(51) Int. Cl.[7]	Id. No.	F1		Theme Code (ref.)
H01M 4/52		H01M 4/52		5H021
2/16		2/16	P	5H028
4/24		4/24	J	5H050
4/32		4/32		
4/62		4/62	C	

Examination request: Not filed   No. of claims: 11   OL (total 12 pages)

Continued on the last page

(21) Application Number: 2000-174401 (P2000-174401)
(22) Application Filing Date: June 9, 2000
(31) Priority Application: 11-314501
(32) Priority Date: November 5, 1999
(33) Priority Country: Japan (JP)
(31) Priority Application: 11-317641
(32) Priority Date: November 9, 1999
(33) Priority Country: Japan (JP)

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(54) [Title of the Invention] NICKEL ELECTRODE ACTIVE MATERIAL FOR ALKALINE STORAGE BATTERY, ALKALINE STORAGE BATTERY, AND METHOD FOR INITIAL CHEMICAL PROCESSING OF ALKALINE STORAGE BATTERY

(57) [Abstract]

[Task] To realized a nickel electrode active material for an alkaline storage battery which is capable of attaining a high charging efficiency, while maintaining a high-rate discharge characteristic, even when the battery temperature is high.

[Means] A nickel electrode active material for an alkaline storage battery comprises a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury. The second component is usually contained in an amount of 0.5-20 parts by weight per 100 parts by weight of the first component.

[Patent Claims]

[Claim 1] A nickel electrode active material for an alkaline storage battery comprising a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury.

[Claim 2] The nickel electrode active material for an alkaline storage battery according to claim 1, wherein said first component is a mixture of at least one selected from nickel hydroxide and nickel hydroxide having a dissimilar element other than the nickel element dissolved therein in the form of solid solution and at least one from metallic cobalt and cobalt oxide.

[Claim 3] The nickel electrode active material for an alkaline storage battery according to claim 1, wherein said first component is a group of particles composed of at least one from a group of particles in which nickel hydroxide particles are coated with a cobalt compound and a group of particles in which particles of nickel hydroxide having a dissimilar element other than the nickel element dissolved therein in the form of solid solution are coated with a cobalt compound.

[Claim 4] The nickel electrode active material for an alkaline storage battery according to claim 3, wherein said cobalt compound is at least one selected from the group composed of cobalt monoxide, divalent α-type cobalt hydroxide, divalent β-type cobalt hydroxide, and compound of high-valence cobalt with a valence higher than two.

[Claim 5] The nickel electrode active material for an alkaline storage battery according to claim 1, 2, 3 or 4, wherein said second component is a compound of said element selected from said group of elements.

[Claim 6] The nickel electrode active material for an alkaline storage battery according to claim 1, 2, 3, 4, or 5, wherein said element selected from said group of elements is a metal element selected from the group composed of holmium, erbium, thulium, and lutetium.

[Claim 7] The nickel electrode active material for an alkaline storage battery according to claim 1, 2, 3, 4, 5, or 6, wherein said second component is contained in an amount of 0.5-20 parts by weight per 100 parts by weight of said first component.

[Claim 8] An alkaline storage battery comprising:

a positive electrode comprising an active material comprising a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury;

a negative electrode having a hydrogen absorbing metal as an active material;

a separator disposed between said positive electrode and said negative electrode;

a case for accommodating said positive electrode, said negative electrode, and said case; and

an electrolytic solution disposed inside said case.

[Claim 9] The alkaline storage battery according to claim 8, wherein said separator is a nonwoven fabric formed by using microfibers of a polyolefin resin system and having hydrophilic properties.

[Claim 10] The alkaline storage battery according to claim 8 or 9, wherein the battery temperature is set to 40-80°C during initial chemical processing.

[Claim 11] A method for initial chemical processing of an alkaline storage battery comprising a step of charging an alkaline storage battery by setting the battery temperature to 40-80°C, said alkaline storage battery comprising a positive electrode comprising an active material comprising a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury; a negative electrode having a hydrogen absorbing metal as an active material; a separator disposed between said positive electrode and said negative electrode; a case for accommodating said positive electrode, said negative electrode, and said case; and an electrolytic solution disposed inside said case.

[Detailed Description of the Invention]

[0001]

[Field of Technology] The present invention relates to an active material, a storage battery, and a method for initial chemical processing of a storage battery, in particular to a nickel electrode active material for an alkaline storage battery, an alkaline storage battery using such as active material, and a method for initial chemical processing of such alkaline storage battery.

[0002]

[Prior Art Technology] Nickel –hydrogen storage batteries, which are the so-called alkaline storage batteries, have found application as power sources for various portable electronic devices such as cellular phones, small power tools, and small personal computers. In nickel-hydrogen storage batteries, a nickel hydroxide-base material is usually used as a positive electrode active material and a hydrogen absorbing alloy is used as a negative electrode active material. Such batteries always featured a high energy density, but in recent years their high-rate discharge characteristic has been improved and they have attracted attention as power sources for high-power applications, e.g., for hybrid automobiles or electric automobiles using electric power and gasoline as energy sources.

[0003] When the above-described nickel-hydrogen storage batteries were used at a temperature close to room temperature, the difference between a potential (oxygen generation potential) at which oxygen is generated due to decomposition of an electrolytic solution and a potential (oxidation reaction potential) at which an oxidation reaction from nickel hydroxide, which is a positive electrode active material, into nickel oxyhydroxide occurs is rather large. As a result, a high charge efficiency can be usually expected. However, if the temperature rises due to heat generation during charge and discharge cycles, this difference in potential decreases and the charge efficiency tends to decrease. For this reason, nickel-hydrogen storage batteries preferably should be used in an environment providing for intensive dissipation of heat and small increase in temperature. However, the batteries are most often used inside narrow spaces in portable electronic devices and automobiles where heat dissipation is inhibited. As a result, temperature increase is impossible to avoid and a high charge efficiency is often difficult to maintain.

[0004] Accordingly various improvements have been researched with the object of suppressing the decrease in charging efficiency under a high temperature in nickel-hydrogen storage batteries. For example, JP-A-3-78965 disclosed a nickel-hydrogen storage battery in which part of the nickel element constituting nickel hydrogen in the positive electrode is replaced with a group II element of the periodic table of the elements, cobalt, or the element and cobalt in order to shift the oxygen generation potential to a higher potential and also to shift the oxidation reaction potential of nickel hydroxide to the lower potential, thereby increasing the difference between the oxidation reaction potential and oxide generation potential even at a high temperature. Furthermore, JP-A-7-45281 disclosed a nickel-hydrogen storage battery in which lithium hydroxide is added to an electrolytic solution of potassium hydroxide, which is the usually used alkali electrolytic solution, with the object of shifting the oxygen generation potential to a higher potential. However, the means for improving the charge efficiency disclosed in those publications do not demonstrate sufficient effect, though they somewhat improve the charging efficiency at a high temperature.

[0005] Further, for example, JP-A-9-92279 disclosed a nickel-hydrogen storage battery in which ytterbium or an ytterbium compound (for example, an oxide such as Yb_2O_3) was added to nickel hydroxide of the positive electrode, this battery having greatly improved high-temperature characteristic. Furthermore, JP-A-5-28992 similarly disclosed a nickel-hydrogen storage battery in which yttrium or an yttrium compound (for example, Y_2O_3 or $Y(OH)_3$) was added to the nickel hydroxide of the positive electrode. In those alkaline storage batteries, the oxygen generation potential during charging was shifted to a higher potential. As a result, the difference between this potential and the oxidation reaction potential could be easily increased and the

charging efficiency at a high temperature could be increased. However, ytterbium, ytterbium compounds, yttrium, or yttrium compounds are usually difficult to disperse in nickel hydroxide. Therefore, it is difficult to obtain a sufficient charging efficiency from the very beginning. Moreover, those elements and compounds sometimes inhibit the formation of an electrically conductive network in the positive electrode, thereby making it difficult to maintain a high-rate discharge characteristic.

[0006] It is an object of the present invention to provide an alkali storage battery in which a high charging efficiency can be attained, while maintaining a high-rate discharge characteristic, even when the battery temperature is high.

[0007]

[Means to Resolve the Problems] A nickel electrode active material for an alkaline storage battery in accordance with the present invention comprises a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury.

[0008] Here, in one embodiment of the first component, it is a mixture of at least one selected from nickel hydroxide and nickel hydroxide having a dissimilar element other than the nickel element dissolved therein in the form of solid solution and at least one from metallic cobalt and cobalt oxide.

[0009] Further, in another embodiment of the first component, it is a group of particles composed of at least one from a group of particles in which nickel hydroxide particles are coated with a cobalt compound and a group of particles in which particles of nickel hydroxide having a dissimilar element other than the nickel element dissolved therein in the form of solid solution are coated with a cobalt compound. Here, the cobalt compound is at least one selected from the group composed of cobalt monoxide, divalent α-type cobalt hydroxide, divalent β-type cobalt hydroxide, and a compound of high-valence cobalt with a valence higher than two.

[0010] On the other hand, the second component is a compound of the element selected from the aforementioned group of elements. The aforementioned element selected from the group of elements is preferably a metal element selected from the group composed of holmium, erbium, thulium, and lutetium.

[0011] In the above-described nickel electrode active material for an alkaline storage battery, the second component is contained in an amount of 0.5-20 parts by weight per 100 parts by weight of the first component.

[0012] The alkaline storage battery in accordance with the present invention comprises a positive electrode comprising an active material comprising a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium,

samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury, a negative electrode having a hydrogen absorbing metal as an active material, a separator disposed between the positive electrode and the negative electrode, a case for accommodating the positive electrode, the negative electrode, and the case; and an electrolytic solution disposed inside the case.

[0013] Here, the separator is a nonwoven fabric formed by using microfibers of a polyolefin resin system and having hydrophilic properties.

[0014] In the alkaline storage battery in accordance with the present invention, the battery temperature is normally set to 40-80°C during the initial chemical processing.

[0015] The method for initial chemical processing of an alkaline storage battery in accordance with the present invention comprises a step of charging an alkaline storage battery by setting the battery temperature to 40-80°C, the alkaline storage battery comprising a positive electrode comprising an active material comprising a first component of a nickel hydroxide system and a second component comprising one element selected from a group of elements composed of scandium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, and mercury; a negative electrode having a hydrogen absorbing metal as an active material; a separator disposed between the positive electrode and the negative electrode; a case for accommodating the positive electrode, the negative electrode, and the case; and an electrolytic solution disposed inside the case.

[0016]

[Description of the Preferred Embodiments] The nickel electrode active material for an alkaline storage battery in accordance with the present invention comprises a first component of a nickel hydroxide system and a second component comprising one element selected from a specific group of elements.

[0017] The first component used in accordance with the present invention, that is, the component, of a nickel hydroxide system is a group of particles that are usually used in alkaline storage batteries such as nickel-hydrogen storage batteries, those particles containing nickel hydroxide as the main component, and no specific limitation is placed on the type of such particles. Here, nickel hydroxide itself or nickel hydroxide in which a dissimilar element other than nickel (that is, other than the constituent elements of nickel hydroxide) is dissolved, forming a solid solution, in the crystal lattice of nickel hydroxide (the nickel hydroxide of the above-described two types will be sometimes referred to hereinbelow as "nickel hydroxide").

[0018] Examples of the dissimilar elements dissolved in nickel hydroxide include zinc and cobalt. Such dissimilar elements are easily dissolved as metals, forming a solid solution, in the crystal lattice of nickel hydroxide, and may be also dissolved in the form of compounds such as oxides or hydroxides in the crystal lattice of nickel hydroxide. Furthermore, two or more dissimilar elements may be dissolved at the same time. Further, it is preferred that the content of

such dissimilar elements in the crystal lattice of nickel hydroxide be usually set to at least 2 parts by weight per weight (sic) of nickel hydroxide.

[0019] Further, with the object of providing nickel hydroxide with electric conductivity and increasing the utilization efficiency thereof, an auxiliary component of cobalt system may be admixed to the above-described main component consisting of nickel hydroxide, as a component of the nickel hydroxide system. A particulate substance (powder) of metallic cobalt or cobalt oxide (usually cobalt monoxide) is an example of such an auxiliary component of cobalt system that can be used herein. Those two components may be appropriately used together. In such a component of a nickel hydroxide system, that is, the first component, an electrically conductive network for increasing electric conductivity is easily formed even after the below-described second component has been admixed, and an active material with good charging efficiency at a high temperature and a high-rate discharge characteristic can be easily obtained.

[0020] Furthermore, the particles of nickel hydroxide or particles of nickel hydroxide having a dissimilar element dissolved therein, which are coated on the surface with a cobalt compound, may be used as the component of the nickel hydroxide system, this coating being used to provide the surface of nickel hydroxide particles with electric conductivity, facilitate the formation of an electrically conductive network in the active material and prevent the shortening of the battery service life caused by the expansion of nickel hydroxide in repeated charging and discharging of the battery. A mixture with an appropriate mixing ratio may be also used. No specific limitation is placed on the cobalt compound to be used for this purpose, provided it is a compound that has been usually used for coating the nickel hydroxide particles employed as the active material with the above-described object. However, the especially preferred compounds include cobalt monoxide, divalent α-type cobalt hydroxide, divalent β-type cobalt hydroxide, and compounds of high-valence cobalt with a valence higher than two. This component of nickel hydroxide system, that is, the first component can easily form an electrically conductive network for increasing the electric conductivity even after the below-described second component has been admixed, and an alkaline storage battery with good charging efficiency at a high temperature and good high-rate discharge characteristic can be easily produced.

[0021] On the other hand, the second component used in accordance with the present invention comprises one element selected from the group of elements including scandium (Sc), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), lutetium (Lu), hafnium (Hf), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), and mercury (Hg).

[0022] In the second component used in accordance with the present invention, no specific limitation is placed on the form in which the element selected from the above-described group of elements is present. Thus, in the second component, the elements selected from the above-described element group may be contained in the elemental form or in the form of a compound. Examples of suitable compounds of the elements include oxides, hydroxides, halogen compounds, and carbonic acid compounds. Furthermore, the compounds of those elements may be in the form of mixtures of compounds containing two or more of such elements. An oxide or hydroxide of the element of the above-described group is the preferred compound.

[0023] A group including Ho, Er, Tm, and Lu (sometimes referred to hereinbelow as "specific element group") of the above-described elements is the preferred for the second component used in accordance with the present invention. It is even more preferred that Er, Tm, and Lu be used as individual metal elements of compounds of those metal elements. A nickel electrode comprising an active material using a second component containing those elements, especially oxides thereof, as shown in FIG. 1, demonstrates a difference between the oxygen generation potential and oxidation reaction potential of nickel hydroxide, which is higher than the difference obtained with other elements, at a temperature of 40°C and 60°C. This is apparently because the active material in accordance with the present invention that contains those elements shifts the oxygen generation potential to a higher potential side. Therefore, oxidation and decomposition of water, which is a competing reaction induced at the final stage of changing an alkaline storage battery can be suppressed. As a result, the charging efficiency of the alkaline storage battery at a high temperature can be effectively increased.

[0024] In the nickel electrode active material for an alkaline storage battery in accordance with the present invention, which comprises the above-described first component and second component, the content ratio of the first component and second component is usually preferably such that the second component is present in an amount of 0.5-20 parts by weight per 100 parts by weight of the first component. It is even more preferred that the amount of the second component be 2-5 parts by weight per 100 parts by weight of the first component. When the content ratio of the second component is less than 0.5 parts by weight, the effect of shifting the oxygen generation potential to a higher potential in the alkaline storage battery sometimes decreases and the charging efficiency of the alkaline storage battery can be difficult to increase under high-temperature operation. Conversely, if the content ratio of the second component exceeds 20 parts by weight, there is a possibility that the formation of the electrically conductive network in the first component of the active material will be inhibited. As a result, there is a risk that the high-rate discharge characteristic of the alkaline storage battery will be degraded. Furthermore, because the second component is not directly related to charging and discharging of the active material, the content ratio of the first component decreases correspondingly to the increase in the content ratio of the first component, the absolute amount of the first component decreases accordingly, and the energy density of the alkaline storage battery can be reduced.

[0025] The nickel electrode active material for an alkaline storage battery in accordance with the present invention can be prepared by individually preparing the above-described first component and second component, adding the second component preferably at the above-described prescribed ratio to the first component, and mixing the components uniformly. The active material that was thus prepared is usually mixed with a binder such as carboxymethyl cellulose to obtain a paste, and this paste is coated on a porous nickel substrate to obtain a positive electrode for an alkaline storage battery.

[0026] The nickel electrode active material for an alkaline storage battery in accordance with the present invention is thus prepared by adding the above-described second component to the above-described first component and mixing the components. Therefore, in the alkaline storage battery that uses such an active material, the oxygen generation potential can be shifted to the higher potentials. As a result, the difference between this oxygen generation potential and the

oxidation reaction potential of the nickel-hydroxide-based components, which is the first component, can be set at a high level. As a result, the alkaline storage battery using the nickel electrode active mass in accordance with the present invention has high resistance to the decrease in charging efficiency even at a high temperature and can maintain a high charging efficiency. Furthermore, in the active material in accordance with the present invention, the second component is contained in a state independent from the first component. Therefore, the formation of the electrically conductive network in the first component is not inhibited. As a result, the active material in accordance with the present invention makes it possible to increase the charging efficiency at a high temperature, while maintaining a high-rate discharge characteristic, in the alkaline storage battery.

[0027] An alkaline storage battery of an embodiment of the present invention will be described below with reference to FIG. 2. Referring to this figure, the alkaline storage battery 1 is a nickel-hydrogen storage battery and mainly comprises a case 2 and a positive electrode 3, a negative electrode 4, a separator 5, and an electrolytic solution (not shown in the figure) disposed inside the case 2.

[0028] The case 2 is a cylindrical container having an opening 2a in the upper part thereof. The bottom surface portion of the case is set as a negative electrode terminal. The positive electrode 3, negative electrode 4, and separator 5 are flexible band-like members. The positive electrode 3 and negative electrode 4 are laminated with the separator 5 being therebetween, and the laminate is spirally wound and disposed inside the case 2. After the electrolytic solution has been poured into the case 2, the opening 2a of the case 2 is liquid-tightly sealed with a sealing plate 7 sandwiching an insulating gasket 6. The sealing plate 7 has a positive electrode terminal at the upper surface thereof. The positive electrode terminal 7 is connected to the positive electrode 3 with a collector 9 that electrically connects the sealing pate 7 and the positive electrode 3.

[0029] The positive electrode 3 used in such as alkaline storage battery 1 is prepared by uniformly coating a paste containing the above-described nickel electrode active material in accordance with the present invention on a nickel porous substrate such as a flexible foamed nickel sheet and then drying the coating.

[0030] Furthermore, the negative electrode 4 is prepared by uniformly coating a paste comprising a hydrogen absorbing alloy power and a thickening agent, for example, on a flexible punched copper (illegible) sheet and then drying the coating. The hydrogen absorbing alloy used herein may be of any type that has been used in nickel-hydrogen batteries. For example, it may be an AB_5-type alloy having a $CaCu_5$-type structure, an AB_2-type alloy having a Laves phase structure, such as $MgCu_2$-type or $MgZn_2$-type alloys, AB-type alloys having a CsCl-type structure, and A_2B-type alloys having a Mg_2Ni-type structure.

[0031] The separator 5 is composed of a gas-permeable nonwoven fabric formed by using, for example, polyethylene fibers, polypropylene fibers, or other polyolefin fibers, preferably fine fibers with an average diameter of 3 to 25 μm. The nonwoven fabric preferably has a weight of 40-80 g/m^2. When the fabric weight is set to this range, the nonwoven fabric can provide for gas permeability, more specifically a gas permeability of about 6-40 cc/cm^2/sec, which can suppress the increase in the internal pressure of the alkaline storage battery 1, while effectively

suppressing the movement of hydrogen generated in the hydrogen absorbing alloy of the negative electrode to the positive electrode 3, this hydrogen being generated by the battery reaction. As a result, the occurrence of the reduction reaction caused by hydrogen in the positive electrode 3 is prevented and self-discharge of the alkaline storage battery 1 can be suppressed.

[0032] Furthermore, the nonwoven fabric constituting the separator 5 preferably has hydrophilic properties. The nonwoven fabric having hydrophilic properties can be manufactured, for example, by the method comprising a step of immersing a nonwoven fabric composed of the above-described fibers into a fuming sulfuric acid, thereby conducting sulfonation, or by a method comprising the steps of immersing a nonwoven fabric into a vinyl monomer solution comprising a photosensitizing agent and then illuminating the nonwoven fabric with UV radiation to introduce carboxyl groups therein. Further, a nonwoven fabric having hydrophilic properties can be also obtained when fibers obtained in advance by graft polymerization of a monomer of an acrylic acid system are used as the polyolefin fibers.

[0033] The above-described separator 5 having hydrophilic properties preferably has an ion exchange capability. In this case, the ion exchange capability of the separator 5 is preferably such as to provide for potassium ion exchange quantity of 0.05-1 miliequiv./g. When the separator 5 has such an ion exchange compatibility, various foreign ions such as NO_3^-, NO_2^-, NH_4^+ that are present in the electrolytic solution and transition metal ions that have eluted from the negative electrode 4 can be adsorbed and self discharge of the alkaline storage battery 1 caused by those impurity ion can be effectively suppressed.

[0034] The self discharge of the alkaline storage battery 1 is considered to be caused by the self-decomposition effect of nickel oxyhydroxide (NiOOH) occurring in the active material of the positive electrode 3 during charging of the alkaline storage battery 1 and by the shuttle effect created by the above-mentioned NO_3^-, NO_2^-, NH_4^+ ions, which are the impurities sometimes present in the positive electrode 3, that is, by the process in which NO_2^- ions are oxidized into NO_3^- ions in the positive electrode 3 and at the same time the NO_3^- are reduced into NO_2^- in the negative electrode 4.

[0035] Further, the electrolytic solution used in the alkaline storage battery 1 can be an alkali aqueous solution of a variety of types and no specific limitation is placed thereon. For example, aqueous solutions of potassium hydroxide, lithium hydroxide, and sodium hydroxide can be used.

[0036] The above-described alkaline storage battery 1 in accordance with the present invention uses the above-described nickel electrode active material in accordance with the present invention in the positive electrode 3. Therefore, the oxygen generation potential can be shifted to a higher potential. As a result, the difference between the oxygen generation potential and the oxidation reaction potential of the nickel hydroxide-base component, which is the first component, can be set to a higher level. Therefore, the alkaline storage battery 1 can demonstrate a high charging efficiency, while maintaining a high-rate discharge characteristic, even at a high temperature.

[0037] Further, the above-described alkaline storage battery 1 is usually used by setting the temperature during initial chemical processing at 40-80°C. When the temperature during initial chemical processing is set within this range, the dissolution or dispersion of the second component contained in the nickel electrode active material into the first component in the positive electrode 3 is easily enhanced and the oxygen generation potential is readily shifted to a higher potential. As a result, the difference between the oxygen generation potential and oxidation reaction potential in the alkaline storage battery 1 further increases and the charging efficiency at a high temperature is further increased.

[0038] Further, when the temperature during initial chemical processing is set higher than 80°C, there is a risk of the electrolytic solution leaking from the case 2. Furthermore, corrosion can easily proceed in the hydrogen absorbing alloy in the negative electrode 4. As a result the service life of the alkaline storage battery 1 can be shortened.

[0039] A method comprising the steps of setting the temperature of the alkaline storage battery 2 in the above-described range, charging the battery at a charging current of 1/20 CmA or less for 10 h or less in this state and then further charging for 10 h or more at a charging current of 1/10 CmA or higher can be used as the initial chemical processing method, but other charging methods can be also used, provided that the temperature is set in the above-described manner.

[0040]

[Embodiments] Embodiments 1 to 14

(Manufacture of positive electrode) A powder (A) of nickel hydroxide coated on the surface thereof with α-type cobalt hydroxide and having zinc and cobalt dissolved in the form of a solid solution therein in respective amount of 3 parts by weight and 6 parts by weight and the element compounds (B) shown in Table 1 were mixed at a weight ratio of A : B = 96.5 : 3.5 and a positive electrode active material was obtained. A total of 80 parts by weight of the active material thus obtained was mixed with 20 parts by weight of carboxymethyl cellulose to obtain a paste. The paste was uniformly coated on a nickel porous substrate serving as a collector, following by drying. Then, the porous substrate was press formed and cut to an electrode size for an AA-size battery. As a result, a positive electrode with a capacity of 1500 mAh was obtained.

[0041]

[Table 1]

Table 1

Test Example	Element compound
1	Pr_6O_{11}
2	Nd_2O_3
3	Sm_2O_3
4	Eu_2O_3
5	Gd_2O_3

6	Tb_4O_7
7	Dy_2O_3
8	Ho_2O_3
9	Er_2O_3
10	Tm_2O_3
11	Lu_2O_3
12	HfO_2
13	Re_2O_7
14	IrO_2

[0042] (Manufacture of negative electrode) A paste was prepared by adding a thickening agent to a hydrogen absorbing alloy powder having a $CaCu_5$-type structure and a composition of $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$ (Mm is a misch metal, which is a mixture of rare earth elements such as La, Ce, Pr, Nd, and Sm; same in the below-described embodiments). The paste was coated on a punched copper (illegible) sheet, followed by drying. Then, the punched copper (illegible) sheet was press formed and cut to an electrode size for an AA-size battery. A negative electrode was thus obtained.

[0043] (Fabrication of nickel-hydrogen storage battery) The above-described positive electrode and negative electrode were wound with a separator being therebetween. The separator consisted of a polypropylene nonwoven fabric obtained by graft polymerization of acrylic acid. The resultant electrode assembly was placed into a cylindrical case. An electrolytic solution composed of a mixed liquid obtained by mixing an aqueous solution of potassium hydroxide with a concentration of 6.8 mol/dm^3 and an aqueous solution of lithium hydroxide with a concentration of 0.5 mol/dm^3 was poured into the case and an alkaline storage battery (nickel-hydrogen storage battery) of tubular shape, AA size and sealed configuration was obtained, this battery having a capacity of 1500 mAh.

[0044] Comparative Example 1

A positive electrode was manufactured in the same manner as in the above-described Embodiments 1 to 14, except that no element compound shown in Table 1 was used. A nickel-hydrogen storage battery identical to that of the Embodiments 1 to 14 was then manufactured by using this positive electrode. The capacity of the positive electrode thus manufactured was 1500 mAh.

[0045] Evaluation 1

Nickel-hydrogen storage batteries of Embodiments 1 to 14 and Comparative Example 1 were allowed to stay for 2 h after the electrolytic solution was poured therein and the batteries were sealed. Then, the initial chemical processing was conducted by maintaining the battery temperature at 40°C. After the battery temperature has become 40°C, the battery was charged for 10 h at a charging current of 1/50 CmA, and then for 10 h at a charging current of 1/10 CmA. Following this initial chemical processing, the battery was constant-current discharged to a battery voltage of 1.0 V at a discharge current of 1/5 CmA, thereby implementing the charge-discharge processing of the first cycle. In the charge-discharge processing of the second and

subsequent cycles, the battery was charged at a constant current for 15 h at a charging current of 1/10 CmA and constant-current discharged to a 1.0 V at a discharge current of 1/5 CmA.

[0046] After the above-described charge-discharge cycle processing, once the discharge capacity of each battery has been stabilized, the charging efficiency of each battery was studied at a temperature of 20°C, 50°C, 60°C, and 70°C. The battery temperature was maintained at 20°C, 50°C, 60°C, and 70°C, the charge-discharge cycles were repeated under the same conditions as those of the above-described second and subsequent cycles till the discharge capacity became constant, and the discharge capacity at this time was considered as the charging efficiency. The results obtained are shown in FIG. 3. In FIG. 3, the discharge capacity (charging efficiency) in the case where the constant-current discharging was conducted at a discharge current of 0.2 CmA at a battery temperature of 20°C was used as a reference (100%). The results shown in FIG. 3 suggest that the batteries of Embodiments 1 to 14 have a higher resistance to the decrease in charging efficiency than the battery of Comparative Example 1 even when the battery temperature is higher. In particular, in an environment with a temperature of 60°C, the batteries of Embodiments 9, 10, 11 shows an especially high charging efficiency.

[0047] Evaluation 2

The temperature during initial chemical processing of Evaluation 1 was set to 20°C, 40°C, 60°C, and 80°C for the batteries of Embodiment 1 and Comparative Example 1. Then, the charging efficiency of those batteries in the case where the battery temperature was set to 60°C was studied in the same manner as in the case of Evaluation 1. The results obtained are shown in FIG. 4. Data shown in FIG. 4 demonstrate that even when the temperature during initial chemical processing is 20°C, the battery of Embodiment 11 has a charging efficiency much higher than that of the battery of Comparative Example 1. However, when the temperature of initial chemical processing was set to 40°C or higher, the charging efficiency became even higher.

[0048] Embodiments 15 to 17

Positive electrodes were fabricated in the same manner as in Embodiments 1 to 14, except that the compounds shown in Table 2 were mixed at the ratios shown in the same table as the element compound (B) with 100 parts by weight of the powder (A) of nickel hydroxide used in Embodiments 1 to 14. The nickel-hydrogen storage batteries identical to those of Embodiments 1 to 14 were fabricated by using those positive electrode.

[0049] Evaluation 3

Initial chemical processing was conduced at a temperature of 40°C with respect to each battery of Embodiments 15 to 17 by the method identical to that used in Evaluation 1. Then, the charging efficiency under a temperature environment of 60°C was studied in the same manner as in Evaluation 1. The results obtained are shown in Table 2. Table 2 demonstrates that when the element compound (B) was admixed within a range of 0.5 to 20 parts by weight to 100 parts by weight of the nickel hydroxide powder (A), the charging efficiency was higher than that obtained without such an element compound (B) (Comparative Example 1; see FIG. 4).

[0050]

[Table 2]

Table 2

Embodiment	Element compound	Mixing ratio (parts by weight)	Charging efficiency (%)
15	Gd_2O_3	0.5	65
		3.5	70
		5	71
		10	68
		20	69
		25	70
1617	Er_2O_3	0.5	86
		3.5	87
		5	88
		10	87
		15	86
		20	86
	HfO_2	0.5	67
		3.5	70
		5	70
		10	71
		20	71
		25	70

[0051] For the battery of Embodiment 16 that was subjected to initial chemical processing at a temperature of 40°C, he mixing quantity of the element compound (B) was further set to 25 parts by weight and the high-rate discharge characteristic was studied under a temperature environment of 20°C. The results obtained are shown in FIG. 5. Further, the high-rate discharge characteristic was obtained by conducting constant-current charging of the battery for 15 h at a charge current of 1/10 CmA, and then conducting constant-current discharge to 1.0 V at a discharge current of ½ CmA, 1 CmA, and 3 CmA. FIG. 5 shows that the battery of Embodiment 16 demonstrated a high charging efficiency (see Table 2) when the mixing ratio of the element compound (B) exceeded 20 parts by weight, but the high-rate discharge characteristic decreased. This is apparently because when the element compound (B) is admixed in an amount of more than 20 parts by weight, the formation of the electrically conductive network in the positive electrode becomes insufficient and the energy density of the battery decreases.

[0052] Embodiment 18

(Manufacture of positive electrode) A first component, 95 wt.%, composed of nickel hydroxide particle group, in which nickel hydroxide particle having zinc and cobalt dissolved therein were coated with cobalt hydroxide, was mixed with Lu_2O_3, 5 wt.%, as the second component, thereby producing a positive electrode active material.

[0053] Then, the positive electrode active material thus obtained was mixed with a 2% aqueous solution of CMC to prepare a paste. The paste was uniformly coated on a metallic nickel porous substrate having a surface density of 450 g/m^2 and a porosity of about 95% and the coating was dried. The porous substrate was then press formed and cut to the electrode size of an AA-size battery. A positive electrode was thus obtained.

[0054] (Manufacture of negative electrode) A hydrogen absorbing alloy having an AB_5-type structure and a composition of $MmNi_{3.5}Co_{0.75}Mn_{0.4}Al_{0.3}$ was ground by using a wet ball mill and a hydrogen alloy powder with a mean particle size of 25 μm was obtained. Then, a thickening agent (polytetrafluoroethylene) was added to the hydrogen absorbing alloy powder and a paste was prepared. The paste was coated on a punching metal and dried. The punching metal was press formed and cut to an electrode size for an AA-size battery. A negative electrode was thus obtained.

[0055] (Manufacture of separator) Polyolefin fibers of separated type with a mean fiber diameter of 10 μm were wet processed into a sheet and a nonwoven fabric with a specific weight of 50-60 g/m^2 was obtained. The nonwoven fabric was subjected to division processing and refined by a high-pressure water flow method and then pressed in hot-calendar rolls to obtain a thickness of 0.12-0.15 mm and an air permeability of 10-20 $cc/cm^2/sec$. The nonwoven fabric was then immersed into a vinyl monomer solution comprising a photosensitizer and the nonwoven fabric was irradiated with UV radiation. As a result, a separator with carboxyl groups introduced therein was obtained. The quantity of carboxyl groups in the separator, that is, the ion exchange capability was 0.2-0.5 miliequiv./g as the potassium ion exchange quantity.

[0056] (Fabrication of nickel-hydrogen storage battery) The above-described positive electrode and negative electrode were wound with the separator therebetween. The resultant electrode assembly was placed into a cylindrical case. An electrolytic solution composed of a mixed liquid composed of an aqueous solution of potassium hydroxide was poured into the case and an alkaline storage battery (nickel-hydrogen storage battery) of tubular shape having a capacity of 1500 mAh was produced.

[0057] Embodiment 19

A nickel-hydrogen storage battery (capacity = 1500 mAh) identical to that of Embodiment 18 was produced, except that the separator for the battery was prepared by using the nonwoven fabric of Embodiment 18 (prior to subjecting it to carboxyl group introducing processing) and treating it with corona discharge.

[0058] Comparative Example 2

A positive electrode was manufactured in the same manner as in Embodiment 18 by using only the first component (that is, no second component was mixed with the first component). A nickel-hydrogen storage batter (capacity 1500 mAh) was manufactured in the same manner as in Embodiment 18, except that the above-mentioned positive electrode was used.

[0059] Evaluation 4

Nickel-hydrogen storage batteries of Embodiments 18, 19 and Comparative Example 2 were held at a temperature of 20°C, constant-current charged for 15 h at a charge current of 0.1 CmA in this state, and then constant-current discharged to a battery voltage of 1.0 V at a discharge current of 0.2 CmA. After the capacity of each battery has stabilized (after the charge-discharge capacities of each battery have almost matched each other), each battery was constant-current charged for 15 h at a charge current of 0.1 CmA and stored for 1 week in a thermostat at a temperature of 45°C. Within the storage period, each battery was discharged every day to a battery voltage of 1.0 V at a discharge current of 0.2 CmA, while maintaining the battery at a temperature of 20°C, and the residual capacity of the battery was measured. Changes in the capacity retention ratio of each battery during storage were found based on the results obtained. The results are shown in FIG. 6. FIG. 6 demonstrates that the battery of Embodiment 18 had a capacity retention ratio by about 15% higher than that of the batteries of Embodiment 19 and Comparative Example 2 and also had a high resistance to self-discharge.

[0060] Furthermore, the batteries of Embodiments 18, 19 and the battery of Comparative Example 2 were constant-current charged for 15 h at a charge current of 0.1 CmA at a temperature of 70°C and the high-rate charging efficiency was studied by comparing the charge capacity in this process with the charge capacity obtained in the case where charging was conducted under the same conditions at normal temperature (20°C). The results obtained are shown in FIG. 7. In FIG. 7, the charging efficiency at a temperature of 70°C is shown as a ratio to the charging capacity at a temperature of 20°C taken as a reference level (100%). Furthermore, the capacity retention ratio after one-week storage at a temperature of 45°C is also shown in FIG. 7. FIG. 7 demonstrates that because the second component is present in the positive electrode and the separator with the above-described specific properties is used in the battery of Embodiment 18, the capacity retention ratio is superior to that of the battery of Embodiment 19 and both the high-rate charging efficiency and capacity retention ratio are superior to those of the battery of Comparative Example 2.

[0061]

[Effect of the Invention] The nickel electrode active material for an alkaline storage battery in accordance with the present invention comprises a first component of a nickel hydroxide system and a second component comprising one element selected from a specific group of elements. Therefore, an alkaline storage battery can be realized that demonstrates a high charging efficiency, while maintaining a high-rate discharge characteristic, even when the battery temperature is high.

[0062] Furthermore, the alkaline storage battery in accordance with the present invention uses the above-described nickel electrode active substance in accordance with the present invention. Therefore the battery demonstrates a high charging efficiency, while maintaining a high-rate discharge characteristic, even when the battery temperature is high. In particular, when the above-described separator is used as the separator for such an alkaline storage battery, the capacity retention ratio is high and the battery has high resistance to self discharge.

[0063] Moreover, the method for initial chemical processing the alkaline storage battery in accordance with the present invention comprises a step of charging the alkaline storage battery in accordance with the present invention in the prescribed battery temperature range. Therefore, the charging efficiency of the alkaline storage battery at a high temperature can be further increased.

[Brief Description of the Drawings]

FIG. 1 shows the difference between the oxygen generation potential of a nickel electrode having a REM oxide added thereto and an oxidation reaction potential of nickel hydroxide.

FIG. 2 is a cross-sectional view illustrating an embodiment of the alkaline storage battery in accordance with the present invention.

FIG. 3 shows the results relating to Evaluation 1 of the embodiments.

FIG. 4 shows the results relating to Evaluation 2 of the embodiments.

FIG. 5 shows the results relating to Evaluation 3 of the embodiments.

FIG. 6 shows the results relating to Evaluation 4 of the embodiments.

FIG. 7 shows other results relating to Evaluation 4 of the embodiments.

[Keys]

1 alkaline storage battery
2 case
3 positive electrode
4 negative electrode
5 separator

FIG. 1

Ordinate: difference between oxygen generation potential of nickel electrode and oxidation reaction potential of nickel hydroxide (mV)
Abscissa: element

FIG. 3

Ordinate: Charging efficiency (%)
Abscissa: Comparative Example 1, Embodiments

FIG. 4

Ordinate: Charging efficiency (%)
Abscissa: set temperature during initial chemical temperature (°C)
Embodiment 11
Comparative Example 1

FIG. 5

Ordinate: Charging efficiency (%)

Abscissa: discharge rate (C)
Addition of 5 parts by weight of the element compound
Addition of 10 parts by weight of the element compound
Addition of 15 parts by weight of the element compound
Addition of 25 parts by weight of the element compound

FIG. 6

Ordinate: capacity retention ratio (%)
Abscissa: (illegible)
Embodiment 18
Embodiment 19
Comparative Example 2

FIG. 7
Ordinate: capacity retention ratio (%)
Abscissa: charging efficiency at 70°C (%)
Embodiment 18
Embodiment 19
Comparative Example 2

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(51) Int. Cl.[7]	Id. No.	F1	Theme Code (ref.)
H01M 10/30		H01M 10/30	Z

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